

## **Ion exchange properties of casts of the anecic earthworm (*Martiodrilus carimaguensis* Jiménez and Moreno) in a Colombian savanna Oxisol**

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**Summary.** Variable-charge minerals dominate tropical soils. The zero point of charge (ZPC) is a function of the various mineral and organic constituents of a soil and the degree to which they interact determines the expression of variable charge. The ZPC can be affected by the presence of organic matter, modifying the overall charge properties of a soil and thus its ability to retain ions against leaching.

Earthworm casts generally have higher organic matter contents, compared with the surrounding bulk soil. The higher organic matter can induce a shift of the ZPC to lower soil pH, improving the range of charge capacity, cation and anion adsorption, and reducing the risk of leaching. This study analyses the influence of the earthworm *Martiodrilus carimaguensis* Jiménez and Moreno on the shift of ZPC in a native savanna and two improved pastures from the Eastern Plains of Colombia. ZPC was determined for casts and bulk soil by a proton titration method to evaluate the amount of charge on colloidal surfaces with different pH and electrolyte concentrations. In all the systems, the ZPC in casts was displaced to more acid values, increasing the generation and retention of charge at natural pH levels (pH in H<sub>2</sub>O). Compared with the non-ingested soil, the level of exchangeable Al<sup>+3</sup> in casts was reduced and the levels of Ca<sup>+2</sup> and Mg<sup>+2</sup> were increased. Improved pastures increased the difference between ZPC and pH (+42 % to +56 %), compared with native savanna. These results were mainly attributed to the ability of earthworms to concentrate organic matter in their casts when ingesting organic-rich substrates. Modification of the ZPC in casts implies an improvement in the cation exchange capacity that could result in a greater availability and retention of nutrients.

**Key words:** Earthworms, *Martiodrilus carimaguensis*, zero point of charge (ZPC), acid soils

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## Introduction

Soil colloids are mixtures of inorganic and organic polymers produced by weathering processes (Sposito & Schindler 1986). Highly weathered conditions result in greater abundance of oxides of iron and aluminum (oxides and oxyhydroxides), minerals that display surface electrical charge, caused by protonation and deprotonation of surface hydroxyl groups. Clay minerals having this type of charge are termed variable-charge clays. Functional groups as organic polymers (carboxylic, phenolic and enolic), soil organic matter and allophane also contribute to variable charge (Oades et al. 1989).

Variable charges on soil surfaces are greatly affected by ambient conditions, being negative or positive, depending on pH and ionic strength of electrolytes in solution in contact with the polymers, and there will be a particular pH value where net charge will be zero (ZPC). This point represents an equal number of protonated and deprotonated sites on the soil (Van Raij & Peech 1972). The presence of soil organic matter (SOM), itself a variable-charge material, can strongly affect the ZPC and the overall charge properties of a soil and, thus, its ability to retain ions against leaching (Oades et al. 1989).

Variable-charge minerals mainly dominate tropical soils. Maintaining organic matter contents at the highest possible levels can achieve minimum ZPC values, while amendment practices can keep soil pH values at the highest practical levels, such management practices can contribute greatly to the capacity of these soils to retain plant nutrient cations (Oades et al. 1989).

Large invertebrates species, mostly earthworms, termites and ants, have been defined as "soil ecosystem engineers" (Lavelle 1997). In the humid tropics, where neither weathering processes nor vegetation are constant, and where clay minerals play a minor role in the regulation of mineralization, soil fauna become the main regulator of SOM processes (Lavelle & Martin 1992). Soil ecosystem engineers actively regulate the activity of soil microorganisms in the organo-mineral structures they produce (e.g., earthworm casts, termite mounds or ant nests), affecting soil aggregation and soil organic matter dynamics (Lavelle & Martin 1992; Decaëns et al. 1999).

The range of such impacts may be considerable in soils with high earthworm activity. In the savannas, the overall ingestion of soil by the earthworm communities has been estimated at 600–1250 t dry soil ha<sup>-1</sup> yr<sup>-1</sup>, which contained 14–15 t soil organic matter ha<sup>-1</sup> yr<sup>-1</sup> (Lavelle 1978). In the Eastern Plains of Colombia, Jiménez et al. (1998) estimated the cast production in the soil profile (surface and underground casts) by an anecic species to be 14.3 t dry casts ha<sup>-1</sup> yr<sup>-1</sup> in a native savanna and 378 t dry casts ha<sup>-1</sup> yr<sup>-1</sup> in an improved grass/legume pasture. Hence, earthworms may affect the ZPC and charge properties of soil through the organo-mineral structures that they produce (e.g., earthworm casts). The aim of this study was to evaluate the effect of a large anecic earthworm (*Martiodrilus carimaguensis* Jiménez and Moreno) on the ZPC of casts in a native savanna and two improved pastures of a Colombian Oxisol. Effects of earthworm activity on Al, Ca and Mg contents were also determined.

## Materials and Methods

### Study site

The study was carried out at the CIAT-CORPOICA Experiment Station of Carimagua (4° 37' N, 71° 19' W, 175 m.a.s.l.) in the Eastern Plains of Colombia. The annual rainfall ranges from 2100 to 2300 mm, and the mean annual temperature is 26 °C. Soils are well-drained silty clay Oxisols (fine, mixed, isohyperthermic typic Haplustox), with pH (H<sub>2</sub>O) 4.5, Al saturation >80 %, low concentrations of Ca, Mg, K and P (Rao et al. 1993).

Sampling was carried out in three experimental plots, representing three different land use systems: (1) a native savanna (Sav), managed traditionally by burning every year during the dry season; (2) a 17-year-old improved pasture of *Brachiaria decumbens* cv. Basilisk (Bdec); (3) a 17-year-old improved pasture of *B. decumbens* associated with a tropical forage herbaceous legume species *Pueraria phaseo-*

*loides* CIAT 9900 ("Kudzu") (Bdec/Pp). Improved pastures, established on a previous savanna site, were fertilized with ( $\text{kg ha}^{-1}$ ) 44 P, 40 K, 14 Mg and 22 S at establishment and with ( $\text{kg ha}^{-1}$ ) 10 P, 9 K, 92.5 Mg and 11 S each second year for the next nine years (Lascano & Estrada 1989). Stocking rates for improved pastures were one cattle· $\text{ha}^{-1}$  during the dry season and two cattle· $\text{ha}^{-1}$  during the wet season.

### Soil and casts sampling

In Carimagua, the introduction of improved pastures derived from natural savannas resulted in a retention of the original earthworm biodiversity but their biomass was increased by tenfold (4.8 g fresh weight  $\text{m}^{-2}$  in the native savanna) (Decaëns et al. 1994). A large anecic species, *Martiodrilus carimaguensis*, was chosen for this study because it dominates the increased earthworm population and biomass under improved pastures. This earthworm produces large amounts of cast, up to 15 cm in height, on the soil surface that can be easily distinguished from other depositions (Jiménez et al. 1998).

Fresh cast samples of *M. carimaguensis* were marked and isolated in the field under three  $1 \times 1 \text{ m}$  cage boxes, placed at random in each improved pasture, and in a  $4 \times 4 \text{ m}$  area in savanna. Daily fresh cast samples were isolated and maintained in field conditions for 20 days, where the cast samples reached equilibrium with the moisture of the soil. The samples were ground and passed through a 2-mm sieve.

Zero point charge and net electric charge were determined by potentiometric titration curves. Serial titration curves were made using an individual sample (soil or casts) for each point. Four grams of each sample were placed in a 50-ml beaker and appropriate amounts of NaCl, 0.001N HCl, 0.001N NaOH and water were added. The final concentrations of NaCl were 1, 0.1, 0.01 and 0.001N. The beakers were covered to prevent evaporation and were stirred occasionally. After 3 days, the pH was measured. The amount of  $\text{H}^+$  and  $\text{OH}^-$  absorbed by the soil sample, at any given pH value, was taken as equal to the amount of HCl or NaOH added to the suspension minus the amount of acid or base required to bring the same volume and the same concentration on NaCl solution, without the soil sample, to the same pH. The ZPC was considered to be the common intersection point of the titration curves carried out in the presence of four concentrations of NaCl. These curves reflect charge generation on the colloidal surface with varying pH and concentration of NaCl. The net electric charge was calculated from the amount of  $\text{H}^+$  and  $\text{OH}^-$  absorbed in NaCl 10 $^{-1}\text{N}$ , with respect to the ZPC at the natural pH ( $\text{H}_2\text{O}$ ) (Van Raij & Peech 1972). A colorimetric method after acid digestion was used to measure total C contents (Houba et al. 1988). Exchangeable Al, Ca and Mg contents were extracted with KCl 1N and determined by titration and atomic absorption, respectively. pH values were determined in  $\text{H}_2\text{O}$  and KCl 1N.

## Results

Both non-ingested soil and casts showed higher pH values in  $\text{H}_2\text{O}$  than in KCl 1N (Table 1), suggesting that the colloidal surfaces have a net negative charge. For all the samples, the ZPC did not coincide with the zero point of titration (the pH of the samples in a salt solution after three days, before the addition of either acid or base), and was displaced to the positive charge side from 0.26 to 0.37 cmol  $\text{kg}^{-1}$  in soils and from 0.54 to 0.76 cmol  $\text{kg}^{-1}$  in casts (Table 1). Thus charge displacements were significantly larger in improved pastures ( $P < 0.05$ ).

**Table 1.** pH properties of an Oxisol and earthworm casts in different land management.

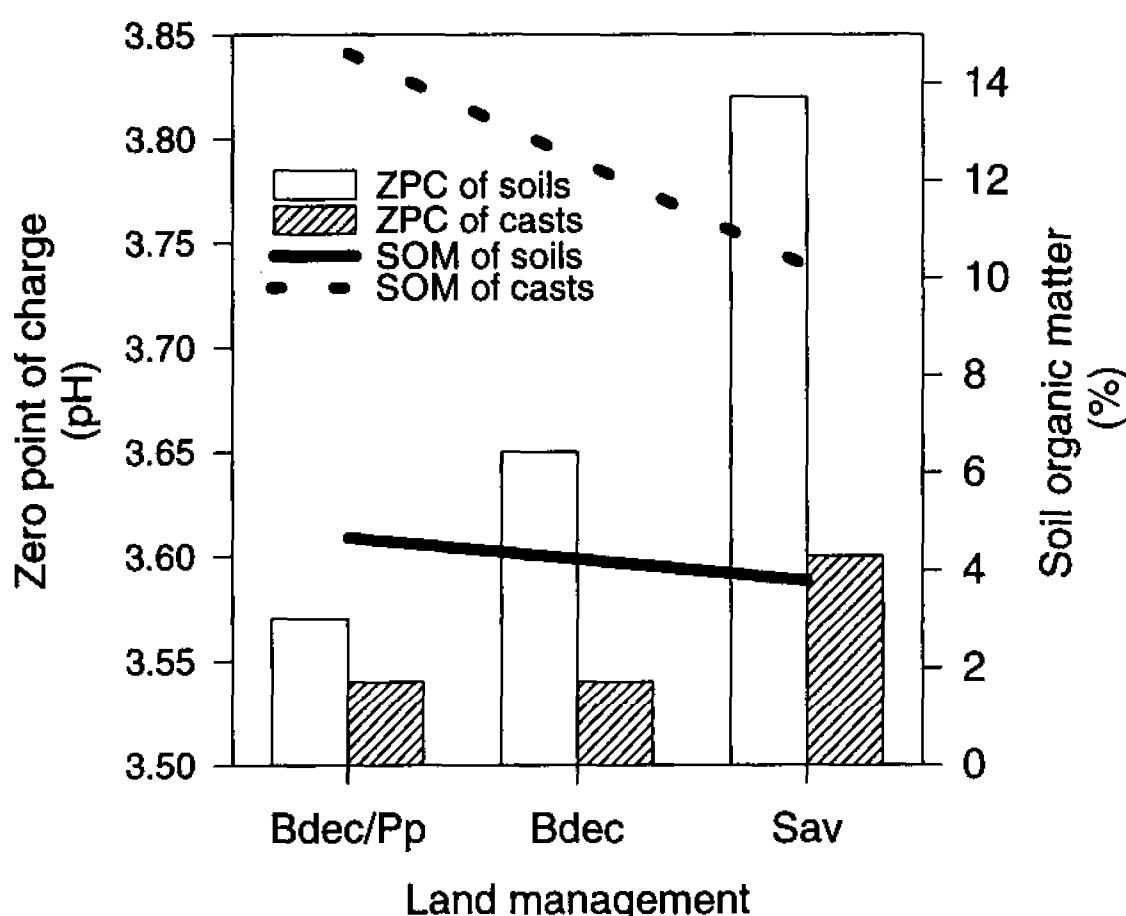
Land use	pH ( $\text{H}_2\text{O}$ )	pH (KCl 1N)	Electric charge displacements <sup>1</sup>	pH-ZPC displacements <sup>2</sup>	Net electric charge <sup>3</sup>
Bdec/Pp, soil	4.98 A	3.79	0.37 C	1.40 A	-0.55 bc
Bdec/Pp, casts	4.94 A	4.00	0.76 A	1.39 A	-0.95 a
Bdec, soil	4.93 A	3.68	0.34 C	1.28 A	-0.62 bc
Bdec, casts	4.91 A	3.84	0.77 A	1.37 A	-1.02 a
Sav, soil	4.72 C	3.77	0.26 C	0.90 B	-0.46 c
Sav, casts	4.87 B	3.80	0.54 B	1.22 A	-0.84 ab

<sup>1</sup> ZPC displacement from the zero point of titration (cmol  $\text{kg}^{-1}$  dry soil)

<sup>2</sup> Distance of natural pH ( $\text{H}_2\text{O}$ ) among ZPC (pH units)

<sup>3</sup> cmol  $\text{kg}^{-1}$  dry soil

Different letters indicate significantly different values. Capitals ( $P < 0.0001$ ), lower case ( $P < 0.05$ )

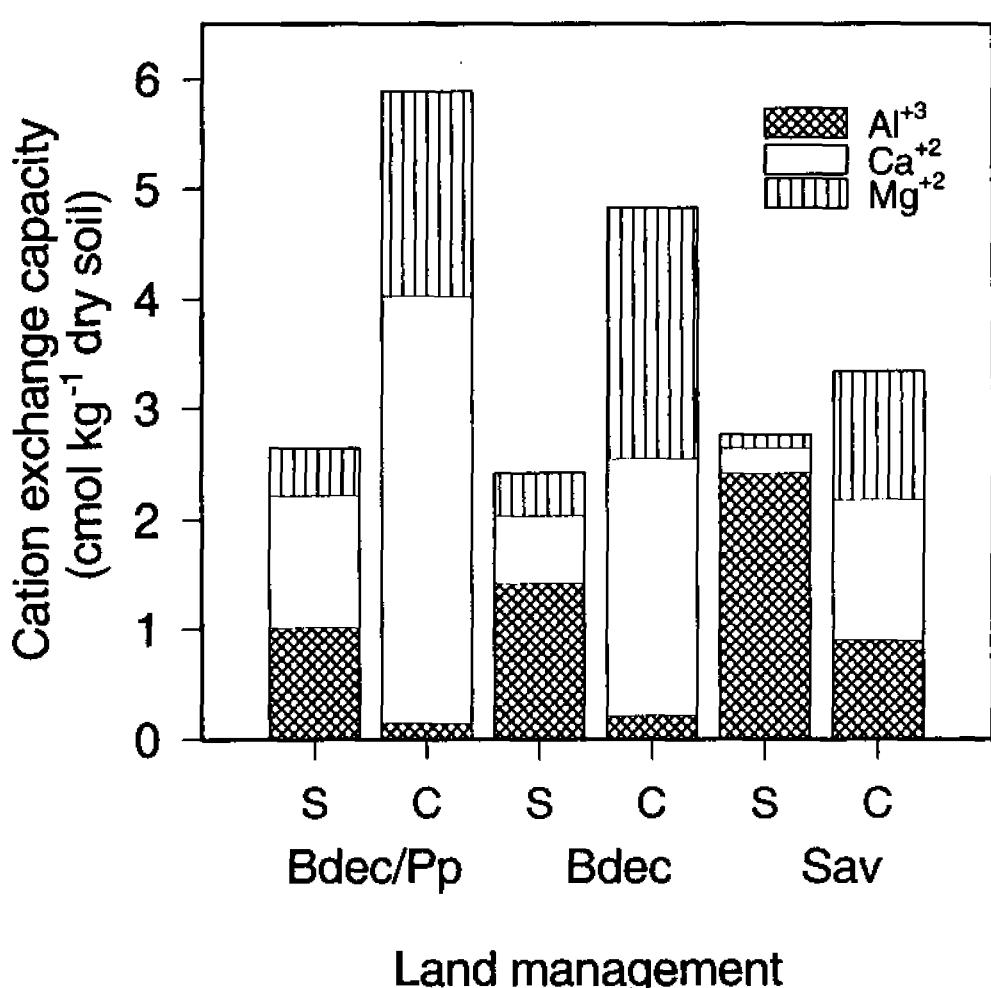


**Fig. 1.** ZPC and soil organic matter (SOM) of an Oxisol and earthworm casts, in different land management. (Net electric charge determined by potentiometric titration with NaCl 0.01N at natural pH ( $H_2O$ )), Bdec/Pp: *Brachiaria decumbens/Pueraria phaseoloides*, Bdec: *B. decumbens*, Sav: native savanna

The pH of the ZPC was lower than the natural pH in each sample (Fig. 1), reflecting an effectively negative net electric charge. In improved pastures the ZPC shifts to low pH values (4.5 and 6.5 % pH units less in the Bdec and Bdec/Pp, respectively), compared with the native savanna (3.82 pH in water). Compared with the bulk soil, ZPC in casts was displaced at lower pH values in both systems (Fig. 1;  $P < 0.05$ ). The higher pH displacements were observed in the savanna (-6%).

The difference among natural pH and ZPC (pH-ZPC) is the main application of ZPC determination. In both improved pastures the pH-ZPC distances were increased by 42 to 56 % in the Bdec and Bdec/Pp, respectively, compared with the native savanna (Table 1,  $P < 0.001$ ). In all experimental plots the pH-ZPC differences were higher in casts than in the bulk soil. The greatest differences were observed in the native savanna (+36 % greater pH-ZPC, comparing with the soil values).

Net electric charge (Table 1) was widely influenced by land use and earthworm digestion ( $P < 0.02$ ). Improved pastures increased the 34 and 19 % (Bdec and Bdec/Pp, respectively) the net electric charges, in comparison to the savanna (-0.46 cmol kg<sup>-1</sup> dry soil). As for pH-ZPC differences and ZPC position, a net electric charge comparison was performed in the savanna



**Fig. 2.** Cation exchange capacity of an Oxisol and earthworm casts, in different land management, s: soil, c: casts, Bdec/Pp: *Brachiaria decumbens/Pueraria phaseoloides*, Bdec: *B. decumbens*, Sav: native savanna

system. In this system, earthworm casts had the greatest increments (82 %), comparing with the non-ingested soil.

The Bdec/Pp or Bdec pastures had a low Al<sup>+3</sup> concentration, and a high Ca<sup>+2</sup> and Mg<sup>+2</sup> content, compared with native savanna ( $P < 0.001$ , Fig. 2). Likewise, soil organic matter (SOM) was increased by 23 to 11 % in Bdec/Pp and Bdec, respectively. Earthworm digestion in each system reduced by 7, 6 and 2 times the Al<sup>+3</sup> concentrations, respectively ( $P < 0.0001$ , Fig. 2). At the same time, Ca<sup>+2</sup> and Mg<sup>+2</sup> contents were increased (e.g., 4 and 6 times in the Bdec pasture). Soil organic matter was enriched by three times in casts compared with the bulk soil in each system. These changes in exchangeable cations resulted in a variation of cation exchange capacity (CEC). Improved pastures increased the CEC of the native savanna by 2 to 4 times (Fig. 2). Likewise, earthworm casts in each system shown greatest increments on CEC (4, 5 and 6 times the CEC in Bdec/Pp, Bdec and Sav, respectively).

## Discussion

The difference between pH determined in water and in 1N KCl is an easy way to know what kind of charge is present in the soil and could be associated with the ZPC. If pH in water is higher than pH in KCl, the soil has negative charge (Van Raij & Peech 1972).

Soil ions (index cation and anions) are called exchangeable if they can be removed or displaced by leaching with other electrolyte solutions. Index ions could be adsorbed with various degrees of affinity to the soil surface and their subsequent removal dependent on the replacement ion used (Oades et al. 1989). Displacement of the ZPC from the zero point of titration is produced by a specific absorption of H<sup>+</sup> and OH<sup>-</sup> in oxidation sites occupied by cations, interlayer H<sup>+</sup> or diluted solids, and is equivalent to the amount of exchangeable Al<sup>+3</sup> (Van Raij & Peech 1972). Oades et al. (1989) found that if ZPC is identified, any excess adsorption of exchangeable cations or anions at this pH could be attributed to permanent charge.

Changes in soil fertility (higher amounts of Ca<sup>+2</sup>, Mg<sup>+2</sup>, SOM, reductions in exchangeable Al<sup>+3</sup> contents) and the overall charge behaviour (low ZPC values, differences between natural pH and ZPC, and higher CEC and net electric charge) resulting from the introduction and management of improved forage pastures in soils previously covered by native savanna, are consequences of several factors. Among these are: fertilization and liming over 15 years since the establishment of the pasture; the utilization of species with high production of below-ground biomass, the contribution of high quality legume-derived SOM, and the stabilization of chemical and physical process by soil faunal activities especially earthworms (Gijsman & Thomas 1995; Rao et al. 1993).

Guggenberger et al. (1995) found that in Carimagua soils, the introduction of *Brachiaria decumbens* alone or associated with *Pueraria phaseoloides* into savanna ecosystems, increased the total C content by 18% in the soil, especially in the clay aggregates. They also explained that changes in agricultural management practices in highly weathered soils could influence the amount, the rate of turnover and the distribution of SOM in different soil aggregates among labile and stable pools. This may explain the observed shift of the ZPC to lower pH values.

The importance of earthworm effects on soil fertility and electrochemical behaviour depends on the space and time scale considered (Lavelle & Martin 1992). Over short time and space scales, microbial activities are enhanced in the earthworm digestive tract, increasing organic matter mineralization, and resulting in an accumulation of assimilable nutrients in the fresh casts. Over a longer time and space scales, dry casts protect organic matter from further mineralization processes, promoting the build up of persistent pools of organic matter in the soil profile (Decaëns et al. 1998). The global impact of *M. carimaguensis* on SOM dynamics may be considerable due to its capacity to ingesting large amounts of soil and fresh OM (up to 378 t ha<sup>-1</sup> yr<sup>-1</sup> at Bdec/Pp system).

Differences in casts between systems probably reflect the litter and SOM quality ingested by the earthworm. Plant litter analysis shown that Bdec and Bdec/Pp derived litter have

higher (two and four times, respectively) contents of  $\text{Ca}^{+2}$ , than the native savanna litter ( $\text{Ca}^{+2} = 0.16 \text{ cmol kg}^{-1}$ ). Likewise,  $\text{Mg}^{+2}$  contents are greater in improved pastures than in native savanna litter (Thomas & Asakawa 1993).

In all systems, large changes in ZPC were observed after soil had transited through the digestive tract of the earthworm. This was especially the case in the savannas, where both SOM and litter quality were the lowest. This suggests the importance of stabilization processes through earthworm activities on soil fertility and electrochemical behaviour in improved pastures, and represents an important means to maintain the soil quality. Oades et al. (1989) demonstrated that maintaining organic matter contents at the highest possible levels to achieve minimum ZPC values would contribute greatly to the capacity of variable charge soils to retain plant nutrient cations and increase CEC. Large differences between natural pH and ZPC could also reduce the risk of cation leaching, and improve by this way the soil sustainability.

## Conclusions

The introduction and management of improved forage pastures in soils previously occupied by native savanna vegetation result in important changes in soil fertility and electrochemical behaviour. Changes in exchangeable cations and electrochemical properties are also significantly improved by earthworm digestion (*M. carimaguensis*) through increments in SOM in their casts. Likewise, the magnitude of these changes depends on the SOM quality consumed by the earthworms (improved pastures associated with herbaceous legumes). Decreases in ZPC values in casts are mainly due to increases in SOM pools and displacement of exchangeable  $\text{Al}^{+3}$ . The changes in soil properties that result from earthworm casting may lead to significant improvement in exchange capacity of infertile Oxisols. This may have implications for the improvement of nutrient retention and recycling in low-input systems.

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